

# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

|   |   |  |
|---|---|--|
| Applicant's or agent's file reference<br>224  | <b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416) |  |
| International application No.<br>PCT/KR 2004/002174   | International filing date (day/month/year)<br>30 August 2004 (30.08.2004)   | Priority Date (day/month/year)<br>20 September 2003 (20.09.2003) |
| International Patent Classification (IPC) or national classification and IPC<br>IPC <sup>7</sup> : B 01 J 29/04 |   |  |
| Applicant<br>KOREA RESEARCH INSTITUTE OF CHEMICAL TECHNOLOGY  |   |  |

|  |  |
|--|--|
| 1. This international preliminary examination report has been prepared by this International Preliminary Examination Authority and is transmitted to the applicant according to Article 36.  |  |
| 2. This REPORT consists of a total of <u>3</u> sheets, including this cover sheet.   |  |
| <input type="checkbox"/> This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT). |  |
| These annexes consist of a total of _____ sheets.  |  |
| 3. This report contains indications relating to the following items:   |  |
| I.   | <input checked="" type="checkbox"/> Basis of the opinion   |
| II.  | <input type="checkbox"/> Priority  |
| III.   | <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability  |
| IV.  | <input type="checkbox"/> Lack of unity of invention  |
| V.   | <input checked="" type="checkbox"/> Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement |
| VI.  | <input type="checkbox"/> Certain documents cited   |
| VII.   | <input type="checkbox"/> Certain defects in the international application  |
| VIII.  | <input type="checkbox"/> Certain observations on the international application   |

|   |  |
|---|--|
| Date of submission of the demand<br>15.04.2005  | Date of completion of this report<br>30 November 2005 (30.11.2005) |
| Name and mailing address of the IPEA/AT<br>Austrian Patent Office<br>Dresdner Straße 87<br>A-1200 Vienna<br>Facsimile No. 1/53424/200 | Authorized officer<br>PUSTERER F.<br>Telephone No. 1/53424/311     |

Form PCT/IPEA/409 (cover sheet) (July 1998)

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# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/KR 2004/002174

## I. Basis of the report

1. With regard to the elements of the international application:\*

☒ the international application as originally filed

☐ the description:

pages \_\_\_\_\_, as originally filed

pages \_\_\_\_\_, filed with the demand

pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

☐ the claims:

pages \_\_\_\_\_, as originally filed

pages \_\_\_\_\_, as amended (together with any statement) under Article 19

pages \_\_\_\_\_, filed with the demand

pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

☐ the drawings:

pages \_\_\_\_\_, as originally filed

pages \_\_\_\_\_, filed with the demand

pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

☐ the sequence listing part of the description:

pages \_\_\_\_\_, as originally filed

pages \_\_\_\_\_, filed with the demand

pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language \_\_\_\_\_ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

☐ the language of publication of the international application (under Rule 48.3(b)).

☐ the language of the translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

☐ contained in the international application in printed form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☐ The amendments have resulted in the cancellation of:

☐ the description, pages \_\_\_\_\_

☐ the claims. Nos. \_\_\_\_\_

☐ the drawings, sheets/fig \_\_\_\_\_

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).\*\*

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as „originally filed“ and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

\*\* Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.  
PCT/KR 2004/002174

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

|                               |        |      |     |
|-------------------------------|--------|------|-----|
| I. Statement                  |        |      |     |
| Novelty (N)                   | Claims | 1-17 | YES |
|                               | Claims | ---- | NO  |
| Inventive step (IS)           | Claims | 1-17 | YES |
|                               | Claims | ---- | NO  |
| Industrial applicability (IA) | Claims | 1-17 | YES |
|                               | Claims | ---- | NO  |

### Citations and explanations (Rule 70.7)

The following documents have been considered for the purposes of this International Preliminary Examination Report:

D1: JP 57-007432 A  
D2: JP 61-017528 A  
D3: US 4590176 A  
D4: KR 2000002477 A

None of the above references D1 to D4, alone or in combination, disclose the present application, as claimed. Therefore, the subject-matter of present claims 1 to 17 is considered to be novel (Art. 33(2) PCT) and the subject-matter of present claims 1 to 17 is considered to involve an inventive step (Art. 33(3) PCT) also.

The claimed application can be industrially applied undoubtedly.

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February 1, 2005

**INFOMRAL COMMENTS**

International Application No.: PCT/KR2004/002174  
Applicant: Korea Research Institute of Chemical Technology

Dear Sir,

In response to the Written Opinion of the International Search Authority dated December 14, 2004, we hereby provide you with our Informal Comments.

Thank you in advance for your cooperation in this matter.

Sincerely yours,



Kyung-Man MIN, Vice-President

for Nam-Hoon PAIK

Int. NHP/KMM/yangjin

Encl. Informal Comments

In response to the Written Opinion dated December 14, 2004 in connection with the PCT/KR2004/002174, consideration of the following remarks is respectfully requested.

#### I. The Present Invention

The present invention relates to a catalyst for preparing dimethyl ether, which comprises (a) hydrophobic zeolite, (b) cation selected from the group consisting of alkali metal, alkaline earth metal and ammonium, and (c) inorganic binder selected from the group consisting of alumina, silica and silica-alumina.

#### II. RE: JP 57-007432 A ('D1' hereinafter) ~ hydrophobic vs. hydrophilic

The conversion reaction of methanol to dimethyl ether is an intermediate step in hydrocarbon synthesis, and thus the yield and the selectivity of the reaction depend on the acidity of a catalyst used, which is already set forth in the originally-filed specification [English specification, p. 3]. For instance, in the presence of a catalyst bearing strong acid sites, methanol, after it is converted into dimethyl ether, is proceeded further to generate hydrocarbons as side products. On the other hand, in the presence of a catalyst bearing weak acid sites, the activity of the catalyst becomes low, thus resulting in low yield of conversion to dimethyl ether. Generally, as  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio increases, hydrophobicity and the strength of acid sites increase. Besides, hydrophilic zeolites are easily deactivated by water, which is contained in reactant or formed during the reaction ( $2\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$ ), because the active sites are easily blocked by water.

According to the present inventors, hydrophilic zeolite is not enough to provide sufficient activity to a catalyst, thus being unable to accomplish desired yield and selectivity, especially at low temperature or in the presence of water. In contrast, a hydrophobic zeolite shows enough catalytic activity, more exactly excess activity, which is controlled by the cation such as alkali metal, alkaline earth metal and ammonium according to the present invention.

For your reference, we hereby provide the following supplemental results, which compare yields between a hydrophilic zeolite-based catalyst and a hydrophobic zeolite-based catalyst.

**Additional Table 1. Methanol as a reactant**

| Example                  | Catalyst                 | SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> | Yield (%)      |             |
|--------------------------|--------------------------|--|----------------|-------------|
|                          |                          |  | Dimethyl ether | Hydrocarbon |
| Example 1 <sup>(1)</sup> | NaH-ZSM-5 <sup>(3)</sup> | 40   | 88.5           | 0           |
| Comp. Ex. <sup>(2)</sup> | NaH-Y <sup>(4)</sup>     | 4.8  | 5.3            | 0           |

(1) Originally-filed Example 1

(2) Catalyst was prepared and the reaction was performed according to the same method as in the originally-filed Example 1 but zeolite was hydrophilic (HY, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 4.8).

(3) **Hydrophobic zeolite**

(4) Hydrophilic zeolite

**Additional Table 2. Water-containing methanol as a reactant**

| Catalyst  | NaH-ZSM-5 <sup>(1)</sup> |             | NaH-Y <sup>(2)</sup> |             |
|---|--------------------------|-------------|----------------------|-------------|
| SiO <sub>2</sub> / Al <sub>2</sub> O <sub>3</sub>   | 50                       |             | 4.8                  |             |
| Temperature   | Yield (%)                |             |                      |             |
|   | Dimethyl ether           | Hydrocarbon | Dimethyl ether       | Hydrocarbon |
| 210 °C  | 63                       | 0           | 0                    | 0           |
| 230 °C  | 84                       | 0           | 0                    | 0           |
| 250 °C  | 83                       | 0           | 1.8                  | 0           |
| 270 °C  | 84                       | 0           | 4.6                  | 0           |
| * Common conditions: Na content: 40 mol % Binder (wt ratio): alumina (1)<br>Pressure: 10 atm LHSV: 10 h <sup>-1</sup><br>Reactant: methanol containing 20 mol% of water |                          |             |                      |             |

(1) Hydrophobic zeolite

(2) Hydrophilic zeolite

### III. RE: JP 61-017528 A ('D2' hereinafter) ~ Inorganic Binder

Meanwhile, the inorganic binder such as alumina, silica, and silica-alumina serves as a diluent to prevent local increase in temperature within a catalyst particle due to hotspot resulted from exothermic reaction processes, thus preventing the generation of hydrocarbon by-products while maintaining an improved yield [English specification, p. 4].

For your reference, we hereby provide the following experimental results, which is already disclosed in the originally-filed Table 1.

Originally-filed Table 1. ~ *Partial citation*

|   | Catalyst   |                   | Yield (%)      |             |
|---|------------|-------------------|----------------|-------------|
|   | Zeolite    | Binder (wt ratio) | Dimethyl ether | Hydrocarbon |
| Ex. 1   | Na-H-ZSM-5 | Alumina (1)       | 88.5           | 0.0         |
| Comp. Ex. 4   | Na-H-ZSM-5 | -                 | 63.4           | 29.1        |
| * Common conditions: Na content: 40 mol %      Pressure: 10 atm<br>LHSV: 25 h <sup>-1</sup> Temperature: 270 °C<br>Reactant: methanol |            |                   |                |             |

#### IV. Conclusive Remarks

As mentioned above, claimed inventions of the present application are novel and inventive over D1 & D2, and thus the patentability of claims 1-7 should be conceded based on the above remarks.